

Cyanide Evaluation

The selection of COPCs is based on a detection frequency greater than 5%, comparison to the USEPA Regional Screening Level (RSL) for tap water, and retention of Class A carcinogens. Through this initial screening process, cyanide is retained as a COPC because of a detection frequency of approximately 7%, reported concentrations greater than the RSL, and the assumption that cyanide occurs in the form of hydrogen cyanide (HCN) which is not a carcinogen. However, the substantial temporal and spatial variability of the detection of cyanide in groundwater at the Site and whether or not the assumption that all or some of the reported concentrations occur as HCN bear further evaluation prior to proceeding to the cyanide risk characterization. For these reasons, the following supplemental evaluation has been conducted.

Spatial and Temporal Variability

The spatial and temporal variability of the cyanide data are illustrated by several observations, as follows:

- The collective data set for cyanide from 2008 to 2016 does not have any concentrations reported above either the New Jersey Groundwater Quality Standard (GWQS) of 100 ug/L or the Safe Drinking Water Act Maximum Contaminant Level (MCL) of 200 ug/L.
- The highest detected concentration of cyanide in groundwater is 21 ug/L at shallow overburden well OB-18, in September 2008. Since 2008, monitoring well OB-18 has been sampled for cyanide twice (2015 and 2016) and both results have been non-detect.
- Other intra-well results show similar non-repeatability including overburden well OB-14A (with four separate sampling events and only one detection), overburden well OB-15B (with three separate sampling events and only one detection), and bedrock well RW-6 (with four separate sampling events and only one detection).
- Two recent sampling events in August of 2015 and August of 2016 included sampling and analysis of groundwater that included cyanide. The results of this sampling (detections only) are shown in the tabulation below.

Monitoring Well	Sample Date	Cyanide, ug/L
OB-9	9/10/10	20
RW-11B (110-100)	9/20/10	2.20
RW-6 (200-210)	9/20/10	0.00
RW-6A (00-00)	9/20/10	0.00
OB-61	9/10/10	0.10
OB-7	9/10/10	10
OB-7	9/21/10	0.00
OB-10B	9/21/10	0.00
RW-11A (110-120)	9/21/10	10
RW-6	9/10/10	1.20
RW-10 (110-01)	9/12/10	1.20

These data again illustrate the substantial variability of the reported cyanide

concentrations, as there is not a single monitoring well that has a cyanide detection in both the 2015 and 2016 sampling events, and the wells are in various locations throughout the Site (e.g., remote from land Areas of Concern [AC], up gradient, etc.). For instance, cyanide has been reported in monitoring wells OB-6 and OB-7 which are over 1,000 feet from any of the land ACs. Another example is monitoring well RW-4A, which is located east of Park Brook and up gradient of both the PMP Area and OCDA. Collectively, these data illustrate that the cyanide detections are not repeatable, they are clearly sporadic, and there is no indication that they are associated with a land AC.

- The above tabulation also shows that in two consecutive, recent sampling events, the cyanide detections are at low, estimated values, with all of the 2016 results “J” qualified (i.e., concentrations are below the method detection level and therefore estimated) and all but two of the 2015 results “J” qualified.

Natural vs. Anthropogenic Sources of Cyanide

Cyanide presence can be attributed to anthropogenic as well as natural sources (e.g., over 2,650 plant species can produce cyanide [ATSDR, 2006]). The levels of cyanide in two common food products illustrate these natural sources of cyanide and concentrations (1) cereal grains: 1-450 ug/Kg, and (2) soy protein (70-300 ug/Kg). Natural biogenic processes of bacteria, fungi, and plants can then release cyanide to the environment (ATSDR, 2006). At the low levels sporadically reported in groundwater at the Site, it is as possible that cyanide is as likely from a natural source as from an anthropogenic source. Relative to the risk characterization, understanding the possibility that risk calculations represent natural conditions is an important consideration.

Analysis of cyanide in groundwater at the Site has been by USEPA Method 9012A for total cyanide, because the groundwater standards for comparison are the NJ GWQS and the MCL which are based on total cyanide. Because of the low levels reported sporadically in groundwater at the Site, and the spatial and temporal variability, it is not feasible to collect samples for speciation analysis to determine the form(s) of cyanide for purposes of the risk characterization. However, the available data can be used to assess likely forms of cyanide.

Form(s) of Cyanide for Purposes of Risk Characterization

The form of cyanide is a determinant in assessing routes of exposure and toxicity factors. Cyanide can be present in the environment as free cyanide, either as hydrocyanic acid (HCN) and/or the cyanide ion (CN⁻), various metal-cyanide complexes, organo-cyanide complexes, and thiocyanates (sulfur compounds). The cyanide ion is highly reactive, behaving as a pseudo-halide (Dzombak et al, 2006). It will readily complex with metals in the groundwater, including potassium, sodium, barium, copper, zinc, iron, cobalt, mercury, as well as alkaline earth metals such as calcium and magnesium (Dzombak et al, 2006). Review of the groundwater monitoring data, including for the 2015 and 2016 sampling events discussed above, indicates that common elements that will complex with the cyanide ion, such as potassium, sodium, calcium, iron, and barium, are routinely present in the groundwater at this Site. As such, to the extent that cyanide could be present as the cyanide ion, it would complex with one or more of these metals that occur in Site groundwater. It is therefore unlikely to occur in the free cyanide ionic form.

If free cyanide is present in an aqueous matrix, the form of cyanide is pH and temperature dependent (Dzombak et al, 2006). The pK_a (acid dissociation constant) for HCN is 9.24,

indicating that, at alkaline pH, the cyanide ion dominates and, in the acidic to neutral pH range, protonated HCN dominates. As temperature decreases, the dissociation of HCN also decreases. Relative to the interpretation of the cyanide data at the Site, the 2016 detections are informative. Below is a tabulation of the most recent August 2016 groundwater data for cyanide reported above detection limits along with corresponding groundwater pH and temperature data:

Monitoring Well	Cyanide, ug/L	pH	Temperature , Deg. C
GW-9	2.0	8.11	11.00
RW-10 (10-100)	2.20	7.0	20.11
RW-9 (200-210)	0.00	8.01	20.01
RW-9A (00-00)	0.00	8.11	11.2
GW-9	0.10	8.01	11.02

As these data illustrate, cyanide was reported over a range of pH and temperature at similar, low-level, and estimated “J” value concentrations. Based on the behavior of cyanide and the geochemistry of the groundwater, one would conclude that cyanide reported in groundwater at well RW-9, the highest of reported “J” values, would most likely be in the form of a metal complex (i.e., cyanide ion would be present and react with one of the commonly detected metals). Consequently, a typical default risk characterization assumption of cyanide presence only in the more toxic, free cyanide form, would not be representative of the actual risk.

HCN is volatile under environmental conditions (Dzombak et al, 2006), has a vapor pressure of 630 mm Hg which is higher than many common organic solvents that are classified as volatile (e.g., carbon tetrachloride – 114 mm Hg, PCE – 19 mm Hg, TCE - 69 mmHg), and is readily volatilized from water at pH values of less than 9 (Dzombak et al, 2006). Looking again at the 2016 cyanide data summarized above as an example, at the neutral to slightly acid pH range, if HCN were present, there is a reasonable probability of loss through volatilization, whereas other forms of cyanide such as the metal- and organo-complexes are more likely to remain in solution.

Overall, the above analysis of cyanide data indicates the following:

- The results of the Site-wide Groundwater RI at the Site indicate that the detections of cyanide in groundwater are not repeatable and they are spatially and temporally sporadic;
- Of the cyanide concentrations reported, the data indicate low levels below both NJ GWQS and MCLs with all concentrations estimated “J” values;
- The data indicate that the source of the estimated “J” value cyanide concentrations is as likely to be natural as it is to be anthropogenic; and
- Regardless of the source (s), cyanide is likely to occur in groundwater at the Site as a metal- or organo-complex rather than as just free cyanide or HCN.

Using the above conclusions, for the purpose of the risk characterization, cyanide is assumed to be present in a combination of free cyanide and the complexed form, with 50% of the cyanide assumed present in the free form, and the remainder as a complex. Despite the abundance of other metals in groundwater at this former mine Site, the selected cyanide complex is thiocyanate, which is the most conservative for risk characterization of the various complexed

forms of cyanide, as it has the lowest tap water RSL other than the free cyanide species. Based on these assumptions, the maximum calculated hazard quotient for cyanide is 1 and the endpoint-specific hazard indices do not exceed a target hazard index for any endpoint evaluated in the risk assessment, and therefore, are within the USEPA's acceptable risk range.